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Cryogenic Preconcentration-Direct FID (Flame
Ionization Detection) Method for Measurement of
Ambient NMOC (Nonmethane Organic Compounds)
Refinement and Comparison with GC
(Gas Chromatographic) Speciation

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Cryogenic Preconcentration-Direct FID Method for Measurement of Ambient NMOC: Refinement and Comparison with GC Speciation

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A method for measuring total nonmethane organic compounds (NMOC) in the atmosphere has been refined to reduce measurement variability and evaluated for possible use in connection with the control of hydrocarbon emissions. The method, a simplification of the conventional gas chromatographic (GC) speciation technique, uses cryogenic preconcentration and flame ionization detection but does not use a GC column. Tests to compare this simplified method to the GC speciation technique, using actual ambient air samples, were carried out. Test results showed that the sensitivity and precision of the simplified method approach those of the speciation technique. Other test results verified that the use of stainless steel sample canisters for collection and temporary storage of NMOC samples is acceptable and contributes little additional variability to the method.

Accurate measurements of ambient concentrations of nonmethane organic compounds (NMOC) are important to pollution control agencies in achieving and maintaining compliance with the National Ambient Air Quality Standard for ozone. NMOC measurements are used together with a simple, empirical photochemical model known as EKMA¹ to develop required ozone control strategies. Until recently, ambient NMOC measurements for this purpose were often obtained with commercial, continuous NMOC analyzers.² However, measurements from these instruments have been shown to be unreliable, particularly at low concentrations, due to a variety of characteristic problems. These problems included the indirect (subtractive) nature of the

measurement process employed,³⁻⁷ nonuniform per-carbon response for different compounds due to oxygen interference,^{6,7} inadequate sensitivity,^{3,4} and interference from water vapor.^{3,4} Although a technical assistance document was prepared to assist users in minimizing these problems,⁸ the usefulness of NMOC measurements obtained with these instruments is limited.

A superior method recommended for measuring ambient levels of NMOC utilizes cryogenic preconcentration followed by gas chromatographic (GC) separation and flame ionization detection (FID).⁹ This technique provides quantitative, identified, species analyses using two chromatographic columns to separate the C₂ to C₁₀ compounds typically observed in ambient air.⁹ The cryogenic sample preconcentration greatly enhances the sensitivity of the method while effectively minimizing interference from methane and oxygen, allowing direct measurement of various organic species with little variation in the per-carbon response for most compounds of interest.

Since species data are not needed for EKMA applications, the GC technique can be simplified by eliminating the

chromatographic separation and measuring the cryogenically preconcentrated ambient sample directly with the FID. Such a method was used by Cox *et al.* to measure NMOC near Louisville, KY and Nashville, TN in 1980.¹⁰ A similar system, using a simple commercial continuous total hydrocarbon analyzer rather than a GC instrument, was described by Jayanty *et al.*^{11,12} in 1982. Where applicable, these methods are much simpler, faster, and considerably easier to use than the GC speciation technique.

Although these simplified methods have performed well in laboratory tests,¹⁰⁻¹² they had not been adequately compared to the GC speciation technique with ambient air samples. Such a comparison is important because the large number and variety of compounds observed in the ambient NMOC measurements, as well as widely varying moisture levels, are difficult to represent adequately in laboratory tests. Jayanty *et al.*¹² reported a limited number of analytical comparisons with the GC speciation technique. Although inconclusive, these comparisons indicated considerably more variability than would be expected from the laboratory tests.

We describe here a number of refinements to the basic analytical system and procedure described by Jayanty *et al.*¹² that were incorporated into the method to improve accuracy and to reduce the measurement variability. Test results are then presented to compare the performance of the refined method to that of the GC speciation technique with measurements of NMOC in typical ambient air samples. Also, additional test results are included to verify

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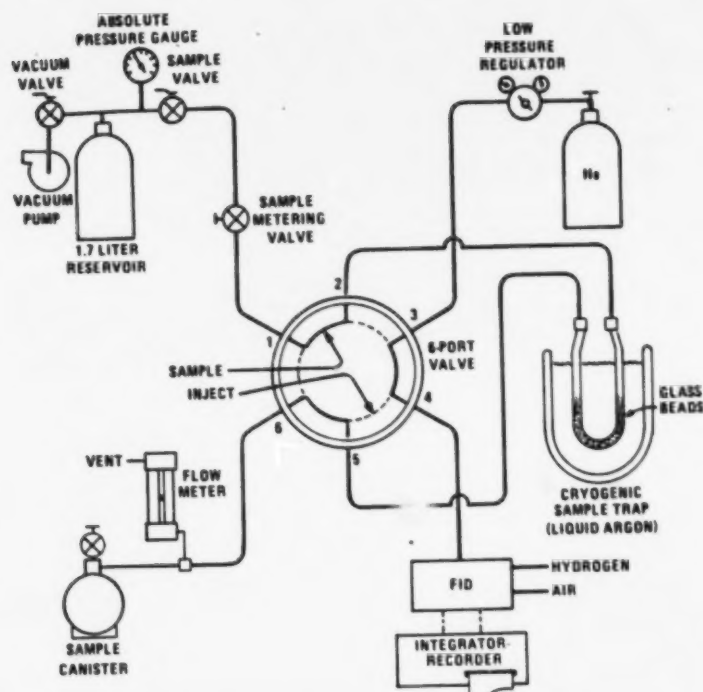


Figure 1. Schematic of system for analysis of total nonmethane hydrocarbons by cryogenic preconcentration and flame ionization detection.

the acceptability of stainless steel canisters for collecting remote air samples for NMOC analysis.

Experimental Methods

Basic Preconcentration-Direct FID (PDFID) Method

Figure 1 shows a schematic diagram of the basic analytical apparatus. Major components include a sample volume metering system, a six-port gas valve (Seisor Model VII, Seismograph Corporation, Tulsa, OK), a cryogenic preconcentration trap, and an FID-integrator-recorder system.

The vacuum pump is first used to reduce the pressure in the 1.7-liter reservoir to a known selected absolute pressure setting, usually about 10 kPa (75 mm Hg). With the valve in the sample (trapping) position, sample air is drawn through the trap, which is immersed in liquid argon (-186°C). The volume of air passing through the trap is measured by the increasing pressure (diminishing vacuum) in the reservoir, and the sample flow is stopped at a second selected pressure. The trap condenses NMOC while permitting air and methane to pass through. During the trapping mode, helium carrier gas passes through the valve directly to the FID.

Following the trapping mode, the valve is switched to the inject position, directing the helium carrier gas

through the trap, in the direction opposite to the previous sample flow, before passing to the FID. The cryogen is then removed, and the trap is heated to approximately 85°C . Organic compounds collected in the trap revolatilize and are swept into the FID by the carrier gas. The resulting peaks are integrated and converted to ppmC by an NMOC calibration curve, prepared using propane-in-air concentration standards. Use of the same precise reservoir pressure readings for each trapping cycle results in a constant sample volume and allows calibration of the system with known concentration standards without quantitatively measuring the actual sample volume.

In the comparison tests, the system was calibrated before and after each day's analyses with propane standards traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM). Each analysis required about 10 min, and three replicate analyses were routinely made on each sample and averaged.

The system described by Jayanty *et al.*¹² utilized a modified commercial total hydrocarbon analyzer. The PDFID method employed a standard GC instrument (Hewlett-Packard Model 5840A, Avondale, PA), which provided an integral peak integrator, FID temperature control, and precision gas flow controls. The GC instrument also provided a convenient means to control the valve and integrator timing, as well as a means to reproducibly heat the

valve and trap, which were mounted inside the GC oven, to release the trapped NMOC. The oven door remained open (and the oven unheated) during the trapping mode. As soon as the liquid cryogen was removed from the trap in the inject mode, the oven door was closed, and the oven rapidly heated to 85°C .

Instead of the unpacked, coiled tubular trap used by Jayanty *et al.*,¹² a 30 cm by 0.32 cm U-shaped trap packed with 60/80 mesh glass beads was used. In preliminary tests, the packed trap provided more repeatable and consistent analyses of test samples than the unpacked, coiled trap.

GC Speciation Method

The gas chromatograph used for speciation was a Hewlett-Packard model 5880A with FID. Hydrocarbons were separated on a 60 m, 0.32 mm I.D. fused silica capillary column (J&W Scientific, Rancho Cordova, CA) with a $1.0\text{ }\mu\text{m}$ thick film of DB-1 bonded liquid phase and programmed from -50°C , held for 1 min, to 120°C at $8^{\circ}\text{C}/\text{min}$ and held at 120°C for 5 minutes. A dual-valve configuration described in detail elsewhere¹³ enabled the routing of sample from a canister through a cryogenic trap and subsequent injection of trap contents onto the column. The cryogenic trap was a 15-cm, 0.32-cm O.D. stainless steel tube packed with 60/80 mesh untreated glass beads. The cryogen used was liquid oxygen (-183°C). Twice-daily calibration of the speciation technique was performed using propane-in-air concentration standards traceable to the same NBS SRM used in the calibration of the PDFID method. Each analysis required about 45 min. The individual species concentrations were summed to obtain the total NMOC concentration.

Ambient Air Sample Canisters

Ambient air samples were collected in 6-liter stainless steel, electropolished canisters (Demaray Scientific Instruments, Ltd., Pullman, WA). A stainless steel metal bellows-type pump (Model 151, Metal Bellows Corporation, Sharon, MA) was used to collect and pump the air sample into the canister to a pressure of approximately 240 kPa (35 psig). Before collecting an ambient sample, each canister was cleaned by alternately evacuating it to a vacuum of $<5\text{ mm Hg}$ absolute and then pressurizing it to 200 kPa (30 psig) with zero air. This cycle was repeated three times. The last fill with zero air was analyzed to verify that the canister was clean before the final evacuation. Some of the canisters were initially heated in an oven at 150°C during the cleaning while others were cleaned at

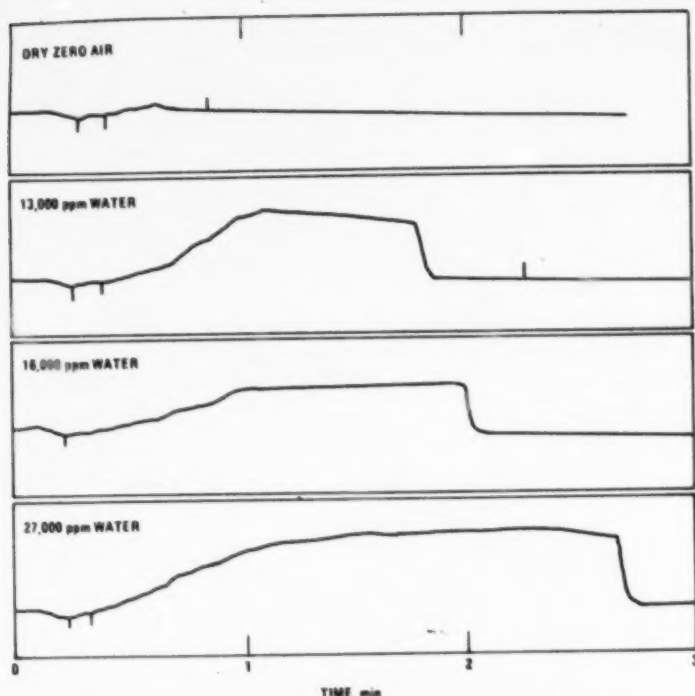


Figure 2. FID baseline shift at various moisture levels (expanded vertical scale).

room temperature. In all cases, the analysis of the final zero air fill showed little difference from direct analysis of the zero air, indicating that the cleaning procedure was effective and reliable. Since no advantage was apparent from heating the canisters during cleaning, the room temperature procedure was adopted.

Results and Discussion

Preliminary tests of the PDFID method indicated markedly poorer precision in the analysis of ambient samples than in analysis of laboratory standards. Similarly, preliminary comparisons of the PDFID method to the GC speciation technique showed greater variation on ambient samples than expected. This difference suggested a problem due to the presence of water vapor, since laboratory standards were prepared in dry air while ambient samples contained considerable moisture. Using an expanded recorder scale, comparison of traces recorded for humidified zero air and for dry zero air clearly indicated a positive shift in the FID baseline caused by moisture. This shift started as soon as the trap was warmed. The degree of the baseline shift seemed to be relatively constant for different levels of humidity; however, the duration of the shift appeared to be roughly proportional to the total moisture content of the sample (see Figure 2). The baseline returned to normal after the moisture had appar-

ently been completely flushed out of the trap by the flow of carrier gas. A typical ambient sample response is shown in Figure 3, where the NMOC response (shaded area) is combined with the (exaggerated) watershifted baseline. This situation can obviously lead to measurement variability due to differences in the amount of water and differences in how the integrator treats the baseline in calculating the area of the peak.

Attempts to dry ambient sample air were not tried due to concern for maintaining the integrity of the air sample mixture. Rather, substantial compensation for the moisture induced baseline shift was achieved by reducing the

integration period of the integrator to 0.9 min (see Figure 3). This value, determined empirically, allowed integration of more than 99 percent of the peak area of the ambient samples tested, while ignoring most of the area caused by the water offset.

A total of 34 ambient air samples were collected, and each sample was analyzed by both the speciation and PDFID methods. Efforts were made to obtain samples representative of three concentration ranges: low (<0.6 ppm C), medium (0.6 to 1.2 ppm C), and high (>1.2 ppm C). The samples were collected between 0700 and 0800 and were analyzed by both methods within 8 hours after collection. Samples in the high concentration range were generally collected near a major roadway carrying heavy truck and automobile traffic. Medium range samples were generally obtained some distance from the roadway, and low range samples were collected in a suburban area away from heavy automobile traffic. The 34 samples were collected in pairs, with the two canisters in each of the 17 pairs being filled simultaneously. The two canisters in each pair were therefore assumed to contain identical air samples. Second (repeat) analyses of 18 of the samples were made with the GC speciation technique, and repeat analyses (set of three) were made for four of the samples with the PDFID method. In these cases, the original and repeat analyses were averaged for the comparison of the two methods.

Figure 4 shows a scatter plot of the PDFID method measurements versus the speciation measurements. As indicated in the diagram, the measured NMOC concentrations ranged from about 0.1 to over 2.0 ppm C. Speciation measurements indicated the general composition of the samples to be approximately 51 percent paraffinic, 17 percent olefinic, and 27 percent aromatic, with the remaining 5 percent of NMOC being acetylene. The results in

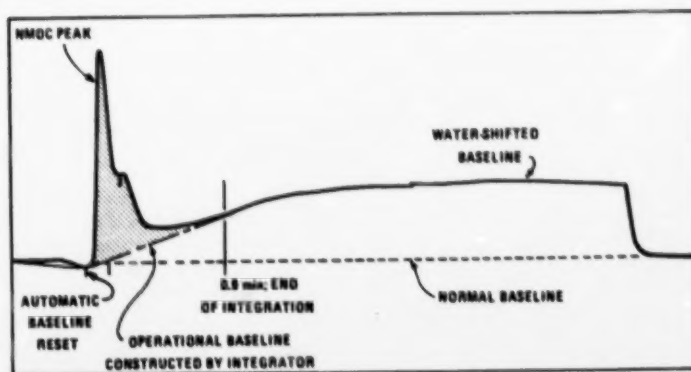


Figure 3. Technique used to minimize water interference. The amount of baseline shift shown is exaggerated with respect to the area of typical ambient NMOC peaks to more clearly illustrate the construction of the operational baseline.

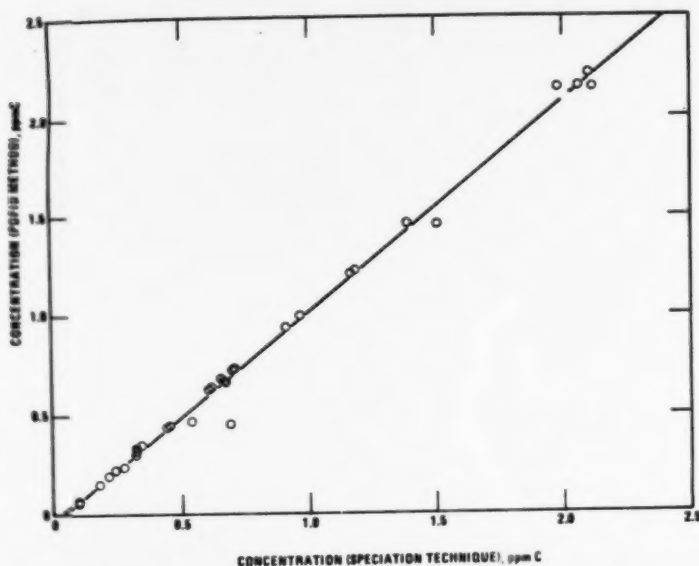


Figure 4. Comparison of PDFID method measurements versus speciation measurements for NMOC analyses of 34 ambient air samples.

Figure 4 suggest a strong linear relationship, which is supported by a strong sample correlation coefficient of 0.99. Regressing the PDFID method values against the speciation method values yielded least squares estimates of -0.033 for the intercept and 1.051 for the slope. A Student's t -test (5 percent significance level) of the intercept and slope indicated that these parameters were significantly different, statistically, from the ideal values of 0 and 1, respectively.

Each observation was individually examined to identify potential outlying observations. Such nonrepresentative observations could exert an excessive effect on the regression analysis. Three possible outlying points were identified, but an investigation of these deviant values failed to produce any physical explanations or violations of the prescribed experimental process. A robust regression analysis described by Huber¹⁶ was used to maintain a realistic analysis of the data while accounting for the possibly deviant values by placing less weight on these observations in the regression analysis. Application of Huber's technique resulted in a reduction of the residual standard deviation (from 0.053 to 0.015), but the intercept and slope estimates changed only slightly, to -0.026 and 1.057 respectively. Again, both of these estimates were found to be significantly different from their ideal values. Assuming the speciation method to be a reference method, the PDFID method was thus observed to have a positive 5.7 percent proportional bias and a negligible fixed bias. It is possible that the 5 percent positive bias is due to the contribution of water vapor. However,

both negative¹⁴ and positive³ effects of water vapor on the flame ionization response have been reported.

Although the biases were found to be statistically significant, compensating correction factors are not proposed or recommended for the PDFID method for two reasons: First, the GC speciation technique is not an absolute reference procedure and is likely to be subject to measurement errors of a few percent. Second, propane was selected for the calibration of both methods because it is believed to be representative of the general mix of hydrocarbon compounds observed in ambient air.^{4,16}

However, the per-carbon responses of the individual hydrocarbon compounds in the mix are expected to vary by a few percent. Consequently, propane cannot be considered an absolute standard.

Analytical method precision for each method was estimated from the respective relative differences of the duplicate analyses. The standard deviation of these relative differences divided by $\sqrt{2}$ provides a recognized estimate of method precision.¹⁷ For the PDFID method, this estimate is 6.2 percent, and for the speciation method, 3.6 percent. Both estimates are well below a commonly acceptable value of 10 percent.

A plot (Figure 5) of the relative standard deviations of the 18 duplicate analyses for the GC speciation technique against concentration shows an inverse relationship with concentration. A power curve ($y = ax^b$) fitted to the data suggests that method precision expressed as a percent of concentration may become considerably larger than 3.6 percent at concentrations below about 0.2 ppm C. A similar finding was observed for the triplicate analyses using the PDFID method (Figure 6). The relative standard deviation was found to vary inversely with concentration, i.e., less than 3 percent at high NMOC concentration to 20.3 percent at low NMOC concentrations. This is consistent with other studies¹⁸ that also found inverse relationships between the coefficient of variation (CV) and concentration level.

As noted previously, it was assumed that nearly identical ambient samples were collected in the paired canisters. An estimate of overall precision based

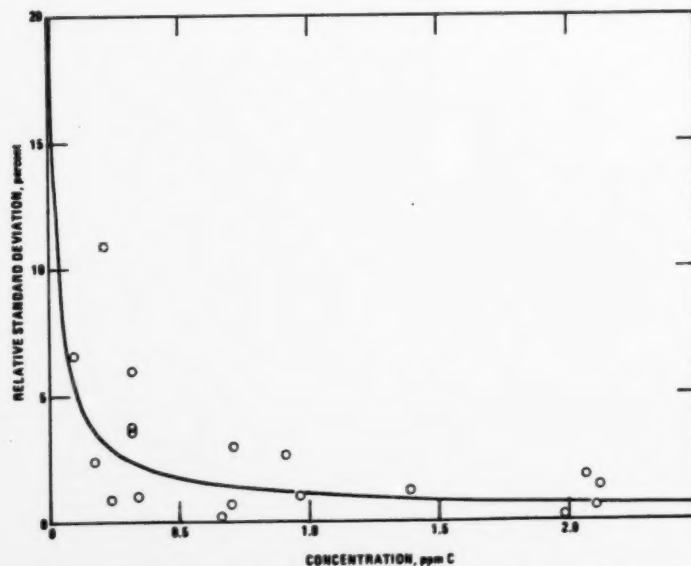


Figure 5. Plot of the relative standard deviations for duplicate analyses of 18 ambient air samples using the speciation technique.

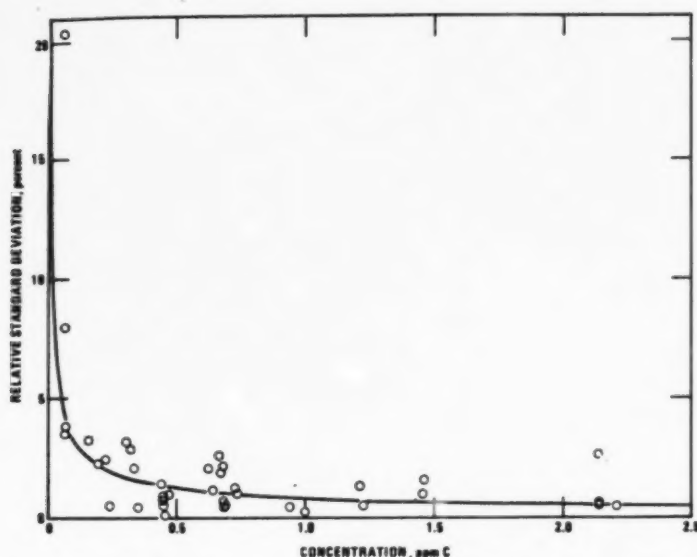


Figure 6. Plot of the relative standard deviations for triplicate analyses of the ambient air samples using the PDFID method.

on the entire experimental process, including any possible effect due to the sample canisters, was obtained from the relative differences of the 17 pairs of ambient samples. For the PDFID method, this precision was estimated to be 4.5 percent, and for the speciation method, 6.0 percent. Thus, including the canister effect increased the imprecision of the speciation method only slightly compared to the analytical precision of 3.6 percent. For the PDFID method, the overall precision estimate of 4.5 percent was less than the 6.2 percent estimate for precision without the canister effect. This unexpected result suggests that the 6.2 percent estimate for precision without the canister effect may be inflated due to the low number of PDFID reanalyses. It also suggests that the canister effect is not large.

To determine longer-term storage effects, selected samples were stored in their canisters for periods of 24 hours and 7 days and reanalyzed with the PDFID method. The results reported in Table I indicate that NMOC concentration changes observed after 7-day storage periods are within the analytical variability of the PDFID method for three of the four tests. This suggests that long-term storage periods for air samples in stainless steel canisters could be considered; however, a more

thorough test evaluation is recommended.

Conclusions

Where nonspeciated measurements of ambient NMOC concentrations are required, such as for use in ozone control modeling via EKMA, the PDFID method appears to be a practical and advantageous choice. When the refinements described here are incorporated and care is used in the peak integration process to minimize water interference, comparative tests have shown that the precision and accuracy of the method closely approach those of the GC speciation technique. Moreover, the method is considerably simpler and faster than the speciation technique. Tests have also shown that the use of pressurized stainless steel canisters for the collection and temporary storage or transport of ambient NMOC samples contributes relatively little additional variability to the measurement of such samples.

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Table I. Stability of ambient samples in stainless steel canisters.

Canister No.	Initial analysis	Analysis after 24 hours		Analysis after 7 days	
		ppm C	%	ppm C	%
5	0.448	0.447	-0.2	0.451	+0.7
6	0.448	0.483	+7.8	0.510	+13.8
7	1.210	1.245	+2.9	1.254	+3.6
8	1.224	1.267	+3.5	1.231	+0.6